

Direct Reduction of $\text{Co}(\text{NO}_3)_2$ leads to Smaller Metal Nanoparticles for Improved FT Activity

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ABSTRACT

Fischer-Tropsch synthesis (FT) converts syngas derived from natural gas, biomass, or coal to a distribution of hydrocarbons that can be upgraded to produce diesel, jet fuels, premium lubricants, and waxes. For the Gas-to-Liquids (GTL) process, cobalt catalysts are used, where activity on a per gram of catalyst basis depends on the surface density of cobalt metal atoms. To increase the Co active site density, cobalt is supported on moderate to high surface area materials, including titania. In comparison with H_2 -activated air calcined 0.5%Pt-12%Co/TiO₂ catalysts, where relatively large Co nanoparticles (NPs) formed, direct reduction of uncalcined catalysts leads to smaller, more strongly interacting Co species. Reduction promoters such as Pt, Re, Ru, and Ag help facilitate their activation, leading to smaller Co NPs and higher Co active site densities.

The BET surface area and porosity characteristics were obtained by Micromeritics 3-Flex system, and this data was used to determine the density and diameter of the pores, as well as size distribution.

Based on temperature programmed reduction x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure spectroscopy (EXAFS) measurements, $\text{Co}(\text{NO}_3)_2$ clusters decomposed to CoO_x species, which oxidized to Co_3O_4 by NO_x , prior to H_2 reduction to CoO , and then Co^0 NPs.

BACKGROUND

Calcination is typically performed to decompose the cobalt nitrate precursor, prior to H_2 -activation. However, it has been found that calcination with certain supports (e.g., SiO_2) leads to agglomeration of cobalt oxides. Therefore, after activation of the cobalt oxides in hydrogen, large cobalt metal NPs are formed, resulting in lower cobalt surface area, and thus lowering the cobalt active site density that participate in FT catalysis. Direct reduction of $\text{Co}(\text{NO}_3)_2$ may lead to smaller cobalt NPs; however, due to the support interaction with cobalt there can be a problem in reducing the cobalt oxide species to the metal. Here, we explore using direct H_2 reduction of $\text{Co}(\text{NO}_3)_2$ and incorporating reduction promoters such as small amounts of Pt, Re, Ru, and Ag to facilitate reduction of the strongly interacting cobalt species.

PURPOSE

The purpose of the project is to test a novel catalyst activation method - direct H_2 -reduction cobalt nitrate precursor - to achieve higher FT activity on a per gram catalyst basis relative to traditional H_2 -activated air calcined catalysts. To be successful, this must be achieved without losing desired catalyst selectivity and stability.

HYPOTHESIS

By utilizing direct reduction of cobalt nitrate precursor on supported Co/TiO_2 catalysts, we believe that reduction of strongly interacting cobalt nitrates will lead to smaller, more strongly interacting Co metal NPs. To facilitate reduction, we also aim to test promoters such as Pt, Re, Ru, and Ag. The aim is to increase Co active site density and thus, activity.

METHODOLOGY

- ❖ **Step 1:** measure the required amount of titania (TiO_2) support
- ❖ **Step 2:** dissolve $\text{Co}(\text{NO}_3)_2$ in H_2O to fill TiO_2 pores.
- ❖ **Step 3:** impregnate the titania until the point of incipient wetness using a buret and a spinning round-bottom flask.
- ❖ **Step 4:** with each loading of the precursor salt, the catalyst must be dried with a rotary evaporator; repeat as needed due to the solubility limit of cobalt nitrate in water.
- ❖ **Step 5:** divide total Co/TiO_2 parent batch into 6 batches.
- ❖ **Step 6:** if a promoter is to be added, dissolve the measured amount in DI water and mix into Co/TiO_2 via buret and a spinning round-bottom flask and dry with rotary evaporator
- ❖ **Step 7:** Then package and label correctly to send to the University of Kentucky Center for Applied Energy Research for testing in continuously stirred tank reactors, and to Argonne National Laboratory for synchrotron experiments.

RESULTS

| Sample | Thermal treatment | A_B (BET) (m^2/g) | V_p (BJH Des) (cm^3/g) | Average D_p (BJH Des) (nm) |
|---------------------------------|----------------------|---------------------------------------|--|------------------------------|
| TiO_2 | uncalcined | 44.5 | 0.36 | 324 |
| | reduced | 11.7 | 0.10 | 197 |
| | air calcined | 40.8 | 0.27 | 243 |
| 12%Co/TiO ₂ | air calcined | 41.4 | 0.26 | 251 |
| | air calcined/reduced | 40.8 | 0.30 | 270 |
| | uncalcined | 15.0 | 0.12 | 215 |
| 0.5%Pt-12%Co/TiO ₂ | reduced | 39.2 | 0.25 | 233 |
| | air calcined | 41.5 | 0.23 | 229 |
| | air calcined/reduced | 40.7 | 0.28 | 243 |
| 0.276%Ag-12%Co/TiO ₂ | uncalcined | 13.5 | 0.11 | 200 |
| | uncalcined | 14.5 | 0.12 | 227 |
| | uncalcined | 11.0 | 0.08 | 126 |

Figure 1. BET surface area and BJH porosity measurements

It is observed that there is little to no pore blocking present in the calcined Co/TiO_2 and $\text{Pt-Co}/\text{TiO}_2$. This is concluded from their pore size of $\sim 41\text{m}^2/\text{g}$. However the uncalcined catalysts suggested significant pore blocking, for they presented surface areas 24% lower than expected. The pore volume of the calcined was much higher than that of the uncalcined, and the pore size distribution was indistinguishable between the two. However, there was no significant difference found between the different thermal treatments regarding the porosity properties.

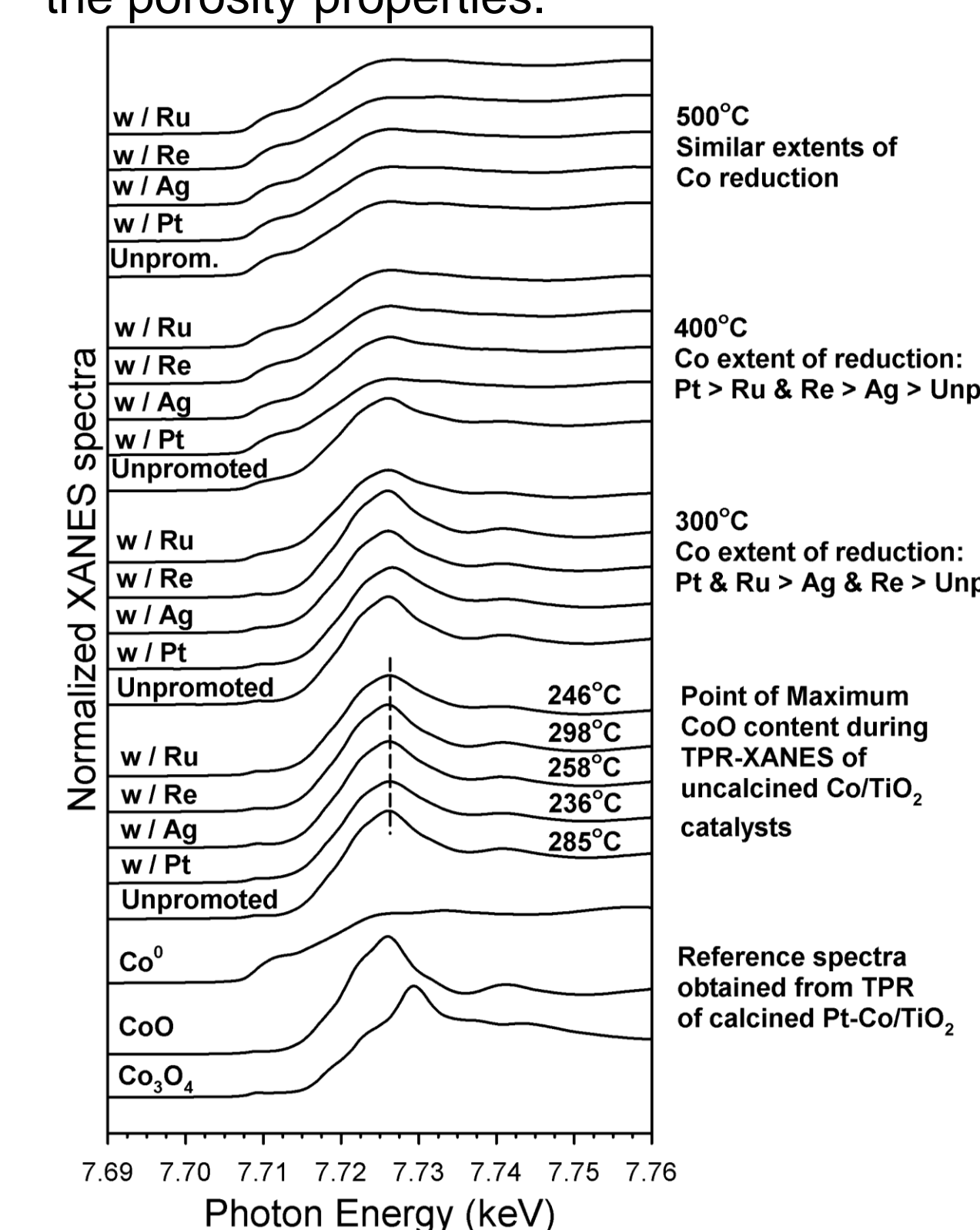
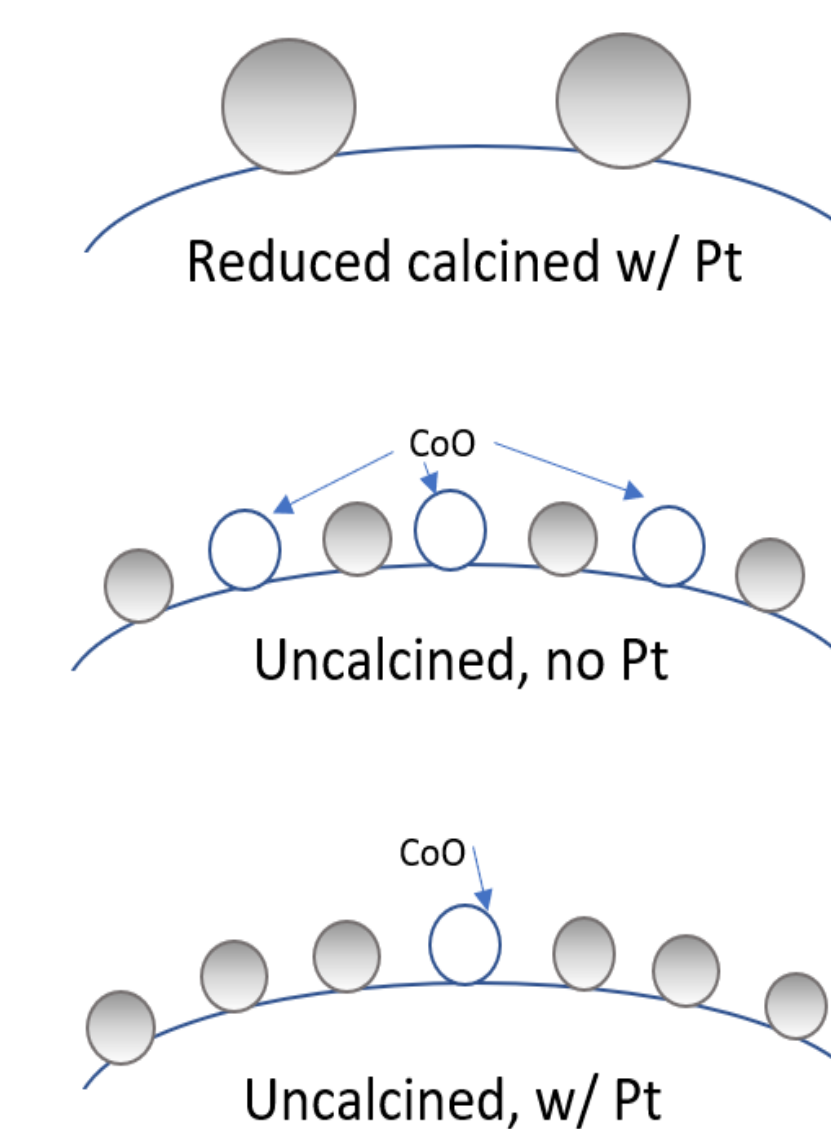


Figure 2. XANES spectra during H_2 TPR.

Standard Reduction, 350°C in H_2

0.5% Pt- 12.5% Co/TiO₂



Surface Co⁰ sites

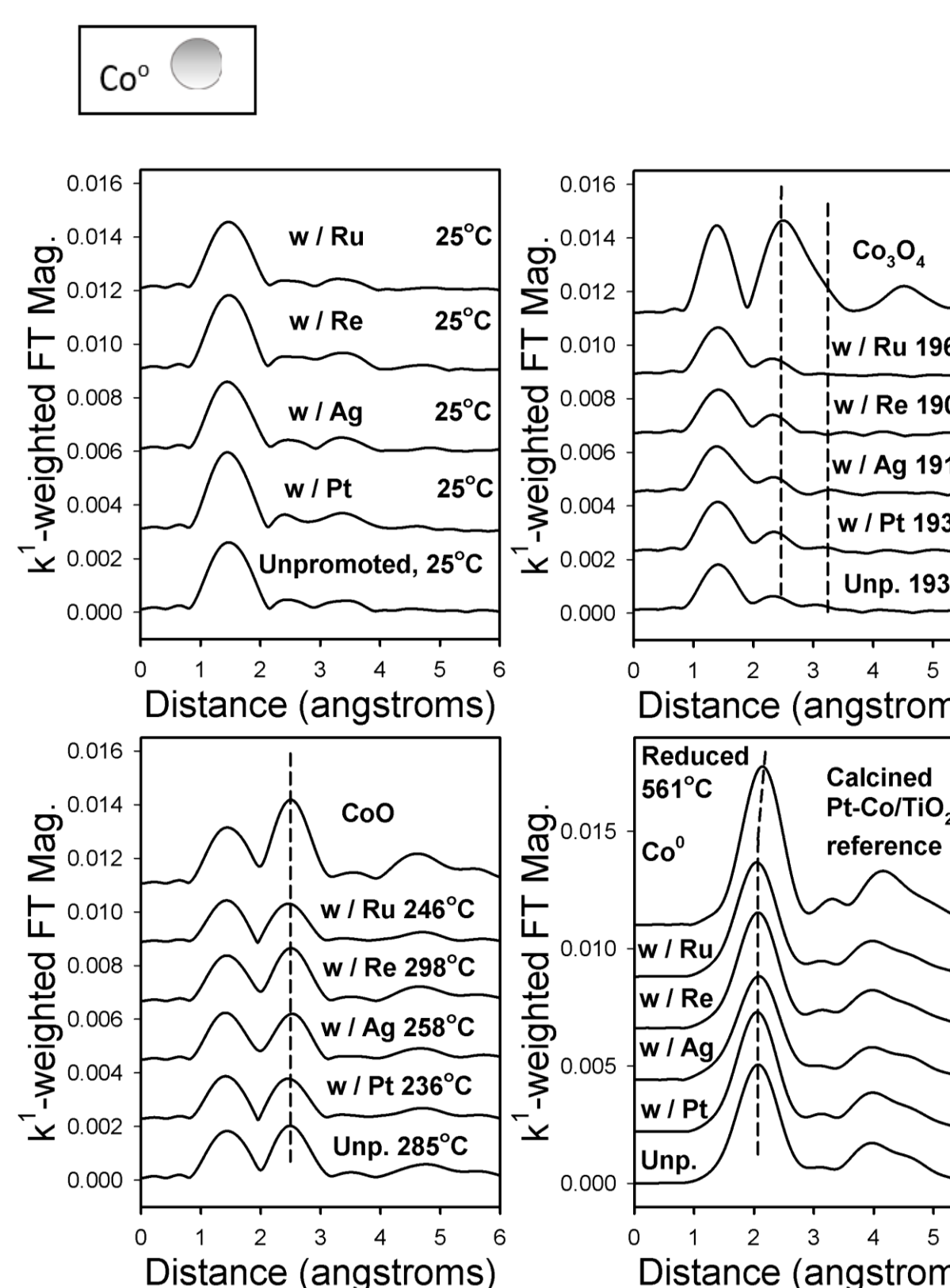


Figure 4. EXAFS spectra of chemical species during H_2 -TPR and fittings of activated catalysts. The much lower $N_{\text{Co-Co}}$ (Co-Co coordination number) of catalysts after direct reduction of cobalt nitrate confirms smaller cobalt NPs than activated calcined catalyst.

CONCLUSIONS

- ❖ The porosity characterizations were not altered by eluding calcination, as the pore density, volume, and BET area were similar after the reduction and passivation
- ❖ XANES experiments confirmed that smaller, more strongly interacting Co species with the titania support, were formed by direct cobalt nitrate reduction as compared to activation of traditional air calcined catalysts.
- ❖ Adding reduction promoters facilitated reduction of these smaller, more strongly interacting Co species, resulting in smaller Co metal NPs as compared to activated air calcined catalysts.
 - ❖ Promoter effectiveness followed the order $\text{Pt} > \text{Re}, \text{Ru} > \text{Ag}$.
- ❖ EXAFS experiments showed that the Co-Co metal coordination number was much lower for Co NPs prepared by direct cobalt nitrate reduction compared with reduced air-calcined catalysts; this confirms that smaller Co NPs were formed, boosting the Co active site density significantly.

REFERENCES

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